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A DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in
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AN IMPROVED COMMUTATOR AND SOME SOURCES OF ERROR IN THE COMMUTATOR METHOD FOR THE MEASUREMENT OF OVERVOLTAGE*

BY A. L. FERGUSON AND G. M. CHEN[1]

Two methods have been extensively used for the measurement of overvoltage commonly known as the direct and commutator methods. Investigators have found that invariably the direct method gives values higher than the commutator method. For more than forty years an explanation has been sought for these observations; and during this time hundreds of researches have been carried out. The explanation offered may be classified into two groups. According to one the discrepancy is due to the existence of a resistance that is different from the ordinary electrolytic resistance between the electrode and the adjacent electrolyte. This resistance has been given various names such as surface resistance, contact resistance, film resistance, transfer resistance, etc. According to the other group the interrupter, which is a necessary part of the equipment for the commutator method, does not permit the measurement of the total discharge potential because of the rapid drop in potential during the interval between the interruption of the current and the measurement of the potential. The question is one of great importance because the values obtained by the two methods in many instances have been found to differ by a large amount and no complete theory of overvoltage, passivity or valve action can be formulated as long as this situation exists.

Several years ago a thorough investigation of this subject was started in this laboratory and has been in progress intermittently since that time. In the first article[2] it was shown beyond any doubt that practically all data obtained with a commutator by previous investigators were open to serious criticism. It was proven that the commutator gives values that are averages over the whole charge or discharge interval. This means that such commutators could never give, directly, values as high as those obtained by the direct method, and offered a possible explanation for the discrepancies between the two methods.

In the second paper[3] an attempt was made to show that the value at the beginning of the discharge interval is the same as at the end of the charge interval; in which case there would be no reason to postulate the existence of transfer resistance. The data all pointed strongly in that direction but the design of the commutator was such that values could not be obtained within 4° of the end of the charge interval, and about 4° of the beginning of

* Contribution from the Chemical Laboratory of the University of Michigan.

[1] Rewritten from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Michigan.

[2] Trans. Am. Electrochem. Soc., **45**, 311 (1924).

[3] Trans. Am. Electrochem. Soc., **47**, 227 (1925).

the discharge interval. The potential was changing so rapidly, particularly on discharge, that it was not safe to extrapolate through these ranges. There were grounds to suspect, also, that the brushes introduced some uncertainties, particularly when the commutator was used at more than one speed.

Before the present work was started the commutator was completely rebuilt with different design to eliminate the difficulties that had been discovered. A new system for the manipulation of the brushes also was employed, which made it possible to explore the region much nearer the end of charge and beginning of discharge than could be done with the old interrupter. In the previous work it was necessary to change the speed of the commutator, which was shown to be a serious disadvantage. By the new arrangement it was not necessary to stop the commutator or change its speed during a complete series of measurements.

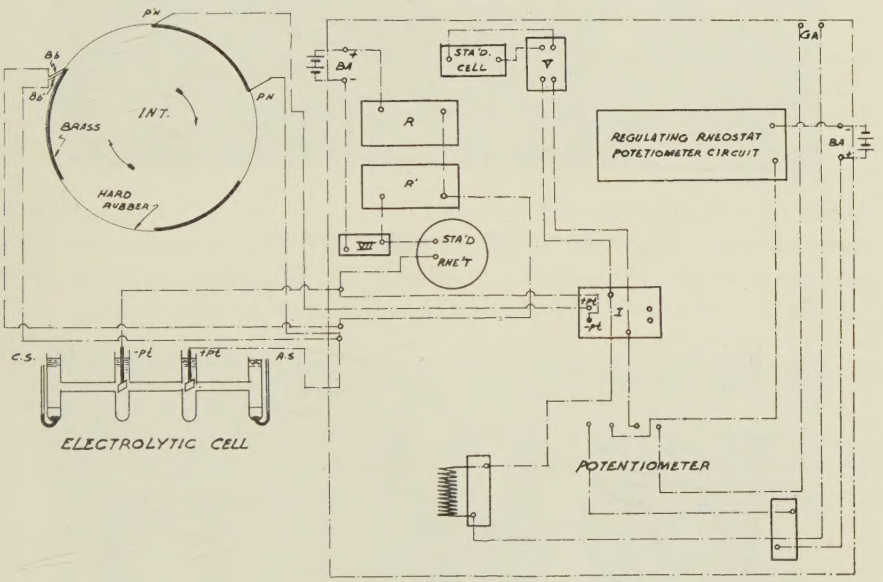

FIG. 1

The essential parts of a potentiometer-commutator assembly for the measurement of decomposition potentials.

Apparatus

The most essential parts of the set-up are shown in Fig. 1. The desired potential, which is obtained as an I.R. drop over resistance R′, may be applied to the cell through the charging brushes (Bb and Bb′), represented in contact with a brass section of the interrupter (Int). The potentiometer is connected to the anode and cathode of the cell through the brushes P_n and P_n' represented in contact with another brass segment near the ends.

The commutator consists of two interrupters directly connected to a $\frac{1}{2}$ horse power motor (see Fig. 2). Each interrupter is made of a disk of hard rubber 2.8 cm. wide and 20 cm. in diameter. The edge is divided into 360°

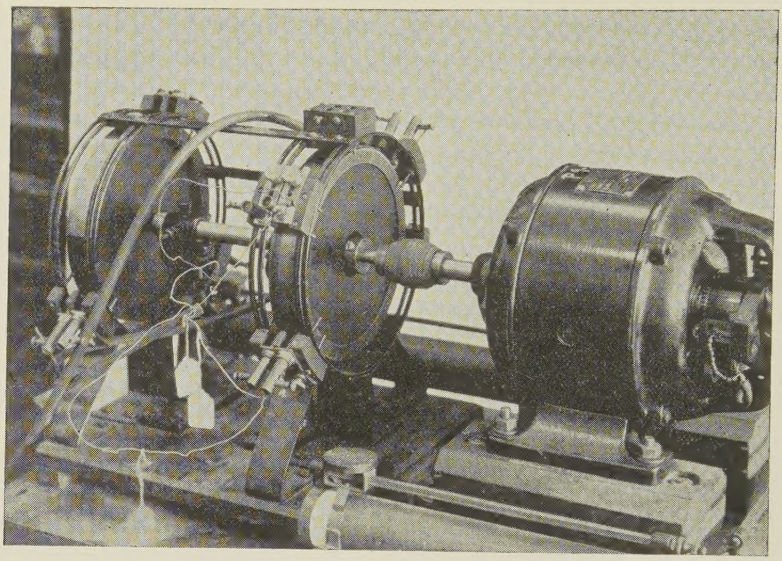

FIG. 2
A direct driven two-disk commutator.

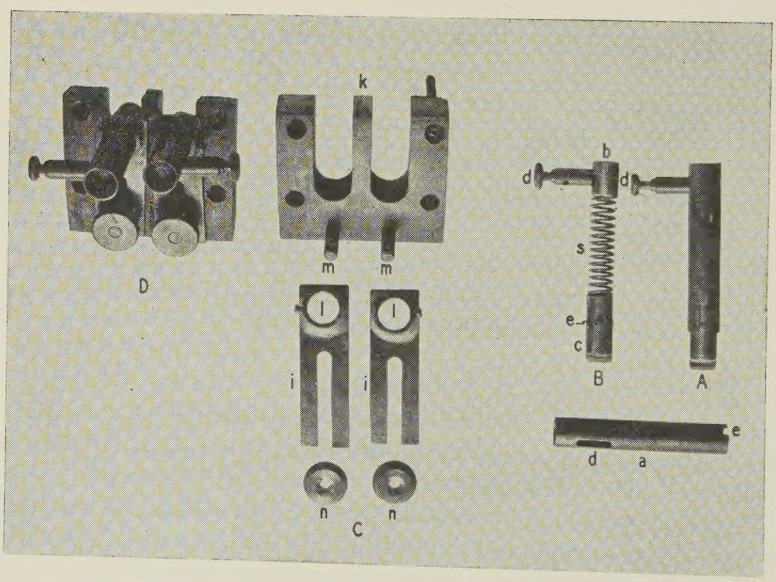

FIG. 3
Brush and brush holder assemblies.

by a scale. In the surface three brass sections each 60° long are set 60° apart, and separated by three hard rubber sections of equal length. The surfaces of the disks are wide enough so that two brushes may be mounted in parallel and thus make contact with the brass segments at the same time. The disks may be shifted to any position on the shaft.

The various parts and the construction of the brushes and brush holders are represented in Fig. 3. The complete brush and holder assembly is shown in (A), and the various parts in (B). The brush proper is made of solid copper of a shape indicated by (c). This is soldered to a spring (S) the other end of which is soldered to a piece of brass (b). The holder (a) is a piece of brass tubing with two narrow openings (d) and (e). The assembly consisting of brush (c), spring (S) and brass piece (b) all slipped inside the holder (a) and held in place by the binding post (d) which passes through opening (d) on the holder. There is a small projection (e) on the brush that fits into the opening (e) and keeps the brush in the proper position. By means of the spring, and the binding post operating in slot (d) the tension of the brush on the interrupter can be changed.

Surrounding each disk of the commutator is an arrangement for supporting the brushes in position (see Fig. 2). Some of the details of a brush support are shown in (C) and (D) of Fig. 3; the various parts are shown in (C) and the assembly in (D). It consists of two parts, the brass strip (i) and the hard rubber support (k). The brass strip has a neck (l) at one end through which the brush assembly (A) may pass; at the other end is a deep slot which enables the brush to be adjusted to any position in the slot of the hard rubber support (k) and held in place by the bolt (m) and nut (n) as illustrated in (D). This whole assembly may be mounted in any position on the frame surrounding the disks as shown in Fig. 2.

The electrolytic cell system is represented diagrammatically in Fig. 1. Two-normal sulfuric acid was used throughout. The reference electrodes were mercurous sulfate and the electrodes in the decomposition cell were platinized platinum.

Experimental

Many experiments were carried out to study such conditions as current density, speed of interrupter, kind of brushes, tension of brushes, length of time commutator was operated, presence of dissolved gases, position of tip of reference electrode, etc. Only a few typical sets of data are recorded, however, in this report.

Table I shows the influence of current density. The time in column (1) is given in seconds from the beginning of the charge or discharge interval. The potentials of the anode against the anode standard are given in column (2); cathode against cathode standard in column (3); the total applied potential minus the I.R. drop through the solution, or, in other words, the sum of (2) and (3) in column (4), the total discharge potential in column (5); and the difference between the total charge potential at the end of charge and the beginning of discharge in column (6). In all experiments conditions were the same except current density and this was made greater in each succeeding experiment.

TABLE I

Comparison of Charge and Discharge Potentials at Different Current Densities

Platinized platinum electrodes. Time is given in sec. after beginning of charge or discharge. The applied potential is greater for each succeeding experiment.

(1) Time $\times 10^{-4}$	(2) $Pt.^+ - A.S.$ (charge)	(3) $Pt.^- - C.S.$ (charge)	(4) $Pt.^+ + Pt.^-$ (3) + (2)	(5) $Pt.^+ - Pt.^-$ (discharge)	(6) End of charge minus beginning of discharge
Experiment (1) Average C.D. = .0006 amp./cm^2					
24	1.126	0.716	1.842	1.855	0.000
end	1.138	0.717	1.855	1.841	
Experiment (2) Average C.D. = .0016 amp./cm^2					
17	1.210	0.726	1.936	1.954	0.000
end	1.228	0.726	1.954	1.936	
Experiment (3) Average C.D. = .0021 amp./cm^2					
11	1.222	0.732	1.954	1.979	0.001
end	1.248	0.732	1.980	1.954	
Experiment (4) Average C.D. = .028 amp./cm^2					
14	1.312	0.758	2.070	2.059	0.069
end	1.369	0.759	2.128	1.984	

The data in column (6) show that at high current densities there is still an appreciable difference between the values for the end of charge and the beginning of discharge. The fact that the agreement is good at low but not at high current densities supports the idea that there is a contact resistance at the interface between electrodes and solution as many investigators have contended. Such a resistance would use up some of the measured charge potential before it reached the electrode. More information on this point is furnished by the data in Table II.

If the differences observed in Table I are due to surface resistances these should be appreciably different at the two electrodes. To test this point the charge and discharge potentials were measured separately for each electrode at a series of current densities. The data are recorded in Table II. Column (2) gives the anode charge potential at the end of charge; column (3), at the beginning of discharge; and column (4) the difference between (3) and (2). Columns (6), (7) and (8) give similar data for the cathode. It should be observed that the differences increase with current density as in Table I. If the differences are due to I.R. drops then the resistances may be obtained by dividing the values in columns (4) and (8) by the corresponding currents. The values thus obtained are recorded in columns (5) and (9).

TABLE II

Anode and Cathode Potentials on Charge and Discharge

(1) Time $\times 10^{-4}$	(2) $Pt.^{+}-A.S.$ (End of charge)	(3) $Pt.^{+}-A.S.$ (Discharge)	(4) Pot. diff.	(5) Resistance	(6) $Pt.^{-}-C.S.$ (End of charge)	(7) $Pt.^{-}-C.S.$ (Discharge)	(8) Pot. diff.	(9) Resistance
Experiment (1) current 0.0024								
0		1.106	0			0.698	0	
9		1.105				0.698		
578		1.098				0.698		
609	1.106				0.698			
Experiment (2) current 0.0086								
0		1.190	0.004	.5		0.732	0.004	.5
8		1.187				0.731		
578		1.157				0.724		
609	1.194				0.736			
Experiment (3) current 0.0143								
0		1.234	0.016	1.1		0.734	0.011	.8
9		1.230				0.733		
660		1.178				0.731		
708	1.250				0.745			
Experiment (4) current 0.0265								
0		1.270	0.027	1.0		0.743	0.019	.8
7		1.265				0.741		
506		1.198				0.736		
543	1.297				0.762			
Experiment (5) current 0.0365								
0		1.283	0.043	1.2		0.745	0.031	.9
8		1.279				0.743		
565		1.193				0.737		
649	1.326				0.776			
Experiment (6) current 0.046								
0		1.295	0.054	1.2		0.744	0.042	.9
9		1.289				0.742		
660		1.196				0.734		
708	1.349				0.786			
Experiment (7) current 0.054								
0		1.316	0.061	1.1		0.747	0.052	.9
8		1.305				0.745		
565		1.203				0.736		
649	1.377				0.799			

The surprising fact is the resistances are practically the same for each electrode and do not change with current density and are, therefore, not due to transfer resistances. In fact it was shown later that the resistances were due to the combined resistances of the electrodes and lead wires of the charging circuit between the electrodes and the points where the potentiometer circuit made contact. In all later work the leads were reduced in length as much as possible and when necessary corrections were made.

To study the nature of the resistance of the commutator brushes an arrangement represented in Fig. 4 was used. The two sets of brushes a and a′ and b and b′ were set 60° apart and in parallel position on the interrupter. The brushes a and b, also, a′ and b′ were connected through the switch I. The potential divider R′ was used as the source of current which passed through the ammeter and either the set of brushes b and b′ or a and a′ depending upon which was in contact with a brass segment. The voltmeter measured the fall of potential over whichever pair of brushes was carrying the current. The voltmeter reading divided by the ammeter reading gave the resistance in the brush contacts.

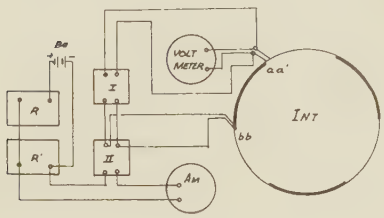

FIG. 4

Diagram of the arrangement for producing a continuous direct current through the brushes of a rotating commutator.

Measurements were taken with three different current densities and various r.p.m.s. and are represented in Fig. 5. The curve shows that the resistance of the commutator brushes increases with increase of r.p.m. but is independent of current density. The results are surprisingly reproducible as shown by the agreement of the three sets of data.

Since, in the commutator method, the current passes through the brushes on the interrupter, an I.R. drop at the contact is inevitable. This drop is very small at low, but is considerable at high current densities, particularly at high commutator speeds. As a result, the applied potential that actually reaches the electrodes from a common source varies with these factors. In other words, the potential from a common source that actually reaches the electrodes is different in the commutator method and the direct method. This subject was studied more fully with an arrangement similar to Fig 4, which permitted the applied potential to be measured in three ways.

The data are recorded in Table III. The first column indicates the method used. In the *direct method* (a) a direct continuous potential was applied to the cell without passing through the interrupter; in the *commutated direct method* (b) a direct continuous potential was applied through the interrupter by two sets of brushes arranged as indicated in Fig. 4; in the *commutator method* (c) a direct intermittent potential was applied through the interrupter which is the regular commutator arrangement; and in the *"direct method"* (d) the system was the same as (a) except a resistance equal to the

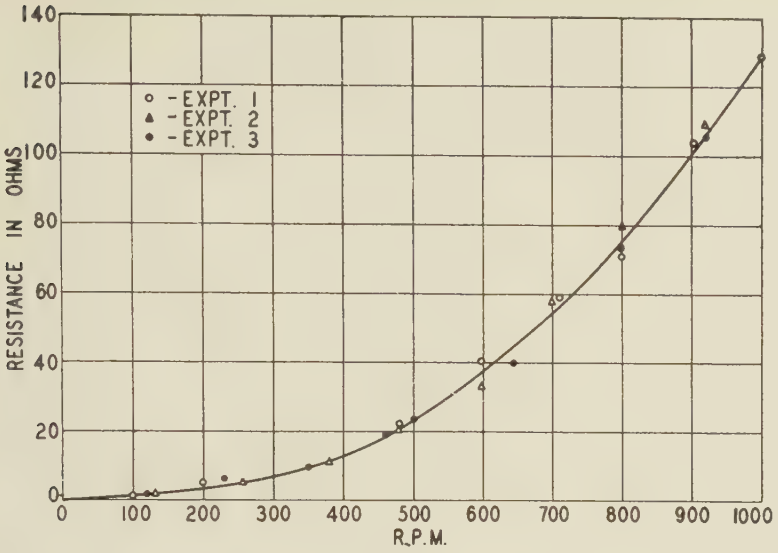

FIG. 5
Curve showing change of brush contact resistance with speed of rotation of commutator.

TABLE III
Comparison of Four Methods for measuring Polarisation

(1) Method	(2) R−R′	(3) Pt.⁺−Pt.⁻ (Charge)	(4) Pt.⁺−A.S. (Charge)	(5) Pt.⁻−C.S. (Charge)	(6) (4) + (5) Pt.⁺−Pt.⁻	(7) Pt.⁺−Pt.⁻	(8) I (Amp.)
Experiment (1)							
(a)	2.037	2.000	1.145	0.734	1.879		0.00338
(b)	2.043	1.995	1.145	0.734	1.879		0.00320
(c)	2.018	1.937	1.121	0.729	1.850	1.850	0.00350
(d)	2.042	1.995	1.145	0.734	0.879		0.00320
Experiment (2)							
(a)	2.322	2.229	1.232	0.750	1.982		0.00844
(b)	2.345	2.200	1.229	0.748	1.977		0.00740
(c)	2.233	2.011	1.210	0.738	1.948	1.943	0.00804
(d)	2.347	2.205	1.230	0.748	1.978		0.00740
Experiment (3)							
(a)	2.498	2.345	1.265	0.757	2.022		0.0136
(b)	2.518	2.298	1.228	0.757	1.985		0.0126
(c)	2.520	2.283	1.219	0.750	1.969	1.946	0.0131
(d)	2.517	2.298	1.226	0.756	1.982		0.0126
Experiment (4)							
(a)	3.084	2.770	1.312	0.768	2.080		0.0273
(b)	3.177	2.789	1.312	0.765	2.077		0.0240
(c)	3.120	2.665	1.289	0.749	2.038	2.015	0.0249
(d)	3.161	2.789	1.312	0.764	2.076		0.0240

brush resistance determined in (b) was inserted in series with the electrolytic cell. The measurements were taken by all four methods at the same time with the same ratio of resistances R′/R of the potential divider used as the source potential. The magnitude of the source potential is given in column (2). In the various experiments all conditions were held constant except the ratio of resistances in the potential divider, and this was changed so as to give a higher source potential for each succeeding experiment.

A comparison of the results in rows (b) and (d) for the various experiments shows that for all measurements made by the commutated direct method (b) and "direct method" (d) the data obtained are practically the same. This indicates that passing the charging current through the resistance of the commutator brushes is equivalent to passing it through a constant carbon resistance. A comparison of the data in rows (a) and (b) shows that in all cases the current (column 8) and also the polarisation (columns 3, 4, 5 and 6) are greater in the direct method (a) than in the commutated direct method (b). This is due to the fact that in the latter the brush resistance is included in the circuit and prevents the total source potential from reaching the electrodes. It may be observed, further, from the data in rows (a), (c) and (b) (column 2) that the source potentials in the former two are less than in the latter though the ratio of resistances on the potential divider is the same. The variation of this common source potential is undoubtedly caused by the change of the apparent resistance of the potential divider as the result of the addition, in the parallel circuit, of the resistance of the commutator brushes in the commutated direct method and by the change of e.m.f. of the cell in these two methods. The resistance of the commutator brushes is of course equal to zero in the direct method.

An inspection of the data in rows (c) (column 8) shows that the current is higher than in (b) and (d) but lower than in (a). It is lower than in (a) because of the added resistance of the brushes and it is higher than in (b) and (d) because it is an intermittent current while in (b) and (d) the current is continuous. An intermittent current of the same value as a continuous one produces less average polarisation. This conclusion is borne out by the observed data recorded in columns 6, 7, and 8 as pointed out above.

These data show that any resistance which develops at the brushes will cause an increase in source potential at the potential divider but will at the same time diminish the charging current; which means that, in a comparison of the direct and commutator methods for measuring overvoltage, the experimenter may apply a certain potential to the cell by the direct method and obtain a certain polarisation potential, then he may apply supposedly this same potential through a commutator and expect that he should get the same polarisation, and in case he does not, he may conclude that the two methods do not give the same value. The data in Table III show that he is not justified in this assumption but rather should expect a lower polarisation, as he actually finds, in the latter case because of the lower current which the data show is always obtained. It is advisable, therefore, in a comparison of the two methods to use a low speed of rotation of the commutator in order to

minimize the resistance of the commutator brushes. It should be pointed out, also, that commutator data obtained at definite intervals of charge or discharge, to be used for extrapolation purposes, must be obtained at the same r.p.m., a point that has not been given sufficient consideration in the past.

Some investigators have contended that in a comparison of the two methods the current densities employed in the two methods should be the same. The data in Table III, columns 6 and 8, show that this conclusion is not true. The current by the commutator method is in all cases slightly higher than by the methods (b) and (d), yet the polarisation is in all cases less. If the current were made equal in the two cases then the difference in polarisation would be even greater, which means that it is not to be expected that the polarisation should be the same by the two methods at the same current density. The reason for this is evident; in the commutator method the current flows intermittently and thus produces less polarisation, or to put it differently, during the time the intermittent current is not flowing the polarisation decreases a little.

Summary

1. A commutator is described which makes it possible to measure charge or discharge potentials within 0.0003 sec. from the beginning or end of the charge and discharge intervals for the electrodes either combined or separately.

2. Several sources of error that may enter into the measurements of polarisation potentials by the commutator method have been pointed out.

THE MEASUREMENT OF POLARISATION BY THE DIRECT AND COMMUTATOR METHODS*

BY A. L. FERGUSON AND G. M. CHEN[1]

In the previous article the authors have described a new commutator which possesses several desirable features and eliminates some of the undesirable features found in other commutators. Some important sources of error, also, were pointed out.

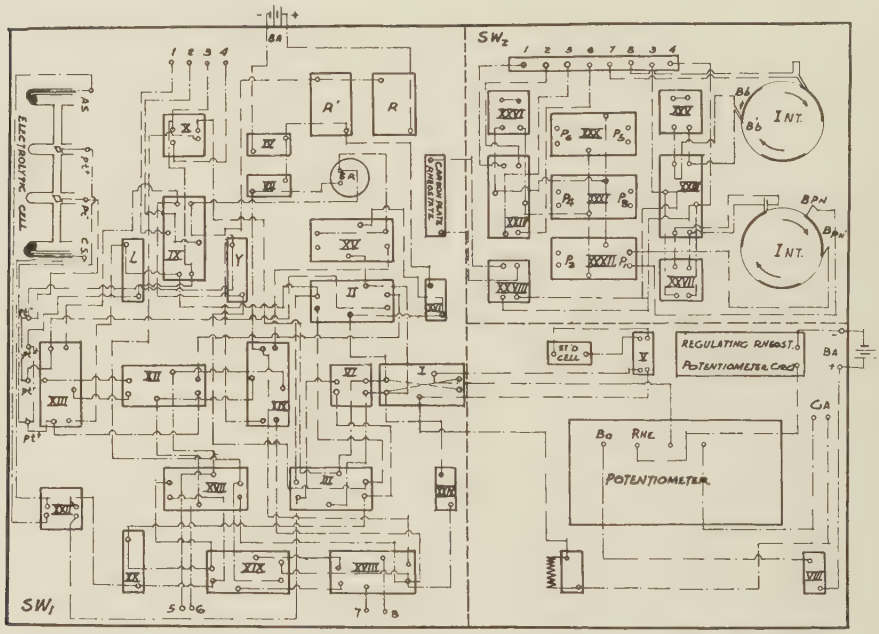

FIG. 1
Complete wiring diagram of switch-board used in polarisation measurements.

In the present work it was found advisable to introduce several additions to the set-up in order to measure the potential over every part of the circuit, even including the lead wires; the object being to make certain that all potentials were correctly measured and that there was no potential or I.R. drop in any part of the circuit unaccounted for. By this arrangement the sum of all the separate potentials in the whole circuit could be checked with the source potentials.

The final system is represented in Fig. 1. A summary of the manipulation of the switches necessary for the more important measurements is given in Table I. To make a measurement, the switches listed following that measurement should be closed and all others opened.

* Contribution from the Chemical Laboratory of the University of Michigan.

[1] Rewritten from a thesis presented in partial fulfillment of the requirement for the degree of Doctor of Philosophy at the University of Michigan.

TABLE I

A. Charge potential with the interrupter rotating.

Switches XXIII and XXIV closed down and P_n closed
(P_n indicates the P_1, P_2, P_3, etc. required)

Potential to be measured	Switches to be closed
Charge	I, II (right), XII (right).
Pt.$^+$—A.S.	I, III (left), XII (left), XIII (down), XXII.
Pt.$^-$—C.S.	I, III (right), XII (left), XIII (up), XXII, XX.
A.S.—C.S.	I, VI, XXII, XVII (left).
Brushes	I, X (right), XIV (up).
S.R.	I, XV (right), XIV (up).
Box Pot.	I, XVI, XIV (down), XXIX.

B. Discharge potentials with interrupter rotating.

Switches XXIII and XXIV closed up and P_n closed

Potential to be measured	Switches to be closed
Discharge	I, II (left), II (down), r.
Pt.$^+$—A.S.	I, III (left), IX (down), XXII.
Pt.$^-$—C.S.	I, III (right), II (up), XX, XXII.

C. Direct method.

Switches XXIII closed up, XXV and XXVI closed

Potential to be measured	Switches to be closed
Charge	I, II (right), XII (right).
Pt.$^+$—A.S.	I, III (left), XII (left), XIII (down).
Pt.$^-$—C.S.	I, III (right), XII (left), XIII (up).
A.S.—C.S.	I, VI, XXII, XVII (left).
Brushes	I, X (right), XVII (right), XXIX.
S.R.	I, XIV (up), XV (right).
Box Pot.	I, XIV (down), XVI, XXIX.

Symbols used for various potentials:

Pt.$^+$—A.S. = anode potential vs anode standard.
Pt.$^-$—C.S. = cathode potential vs cathode standard.
Pt.$^+$—C.S. = anode potential vs cathode standard.
Pt.$^-$—A.S. = cathode potential vs anode standard.
Pt.$^+$+Pt.$^-$ = sum of the single electrode potential of anode and that of cathode.
Pt.$^+$—Pt.$^-$ (charge) = potential, anode vs cathode, including the I.R. drop through the solution.
Pt.$^+$—Pt.$^-$ (discharge) = potential, anode vs cathode, equal to the sum of electrode potentials on discharge.
C.D. = current density.
Box Pot. = common source of potential taken from the potential divider.
Hg.$^+$—Hg.$^-$ or I.R. = I.R. drops through the solution, or potential between two reference electrodes.
Br. = potential across the brushes.
S.R. = potential across the standard resistance.

The electrolytic cell system was changed somewhat from that used before. The new arrangement is shown in Fig. 2. This more complex system was designed to prevent the diffusion of mercurous ions into the decomposition cell from the reference electrodes, and to eliminate any I.R. drop between the electrode of the decomposition cell and the reference electrode. Two normal sulfuric acid was used in all experiments. In some experiments the electrodes were platinized and in others bright.

The heart of the whole equipment is, of course, the commutator. For a description see the previous paper. An end view of one of the interrupters giving considerable detail is shown in Fig. 3.

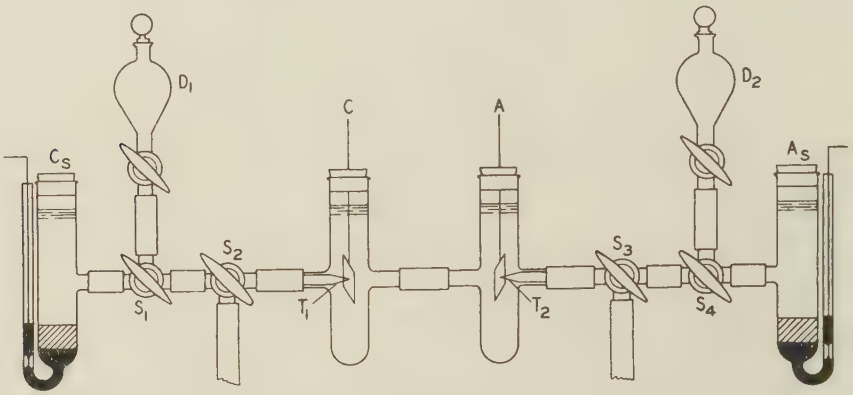

FIG. 2
Cell system for polarisation measurements.

The charging brushes B_b are set in parallel so that both make contact at the same instant. The potentiometer brushes B_{p1} and $B_{p1'}$ are set 59° apart which means they close the potentiometer circuit during only one degree once every 1/3 of a revolution. The potential measured is, then, the average during a time interval equal to $1x(1/360) \times (60/\text{r.p.m.})$ sec. If the interrupter rotates clockwise and has come to the position shown in Fig. 3, the charging brushes have made contact on a brass plate for one degree and during this same time the potentiometer brushes B_{p1} and $B_{p1'}$ have made connection to the potentiometer through switch P_1 in S_{w2} of Fig. 1. The potential measured is the average value of the potentials during only this one first degree of charge, since, after the interrupter has turned more than one degree the connection to the potentiometer is broken at B_{p1}. After 7 degrees, connection is made again for a period of one degree by brushes B_{p2} and $B_{p2'}$. In a similar manner other pairs of brushes are used to measure either charge or discharge or both after any desired known intervals of time at constant r.p.m. and practically simultaneously.

If the potentiometer contact be made for one degree and the potentiometer brushes commence to make connection after the charging brushes have been in contact with the brass section of the interrupter for "d" degrees, then the

time interval after charge starts corresponding to the potential measured is $d - \frac{1}{2}$ degrees or in seconds is given by the expression

$$(d - \tfrac{1}{2})\ (1/350 \times 60/\text{r.p.m.})$$

One might think, at first, that with the apparatus here described it should be possible to reduce the discharge time interval to any desired value by in-

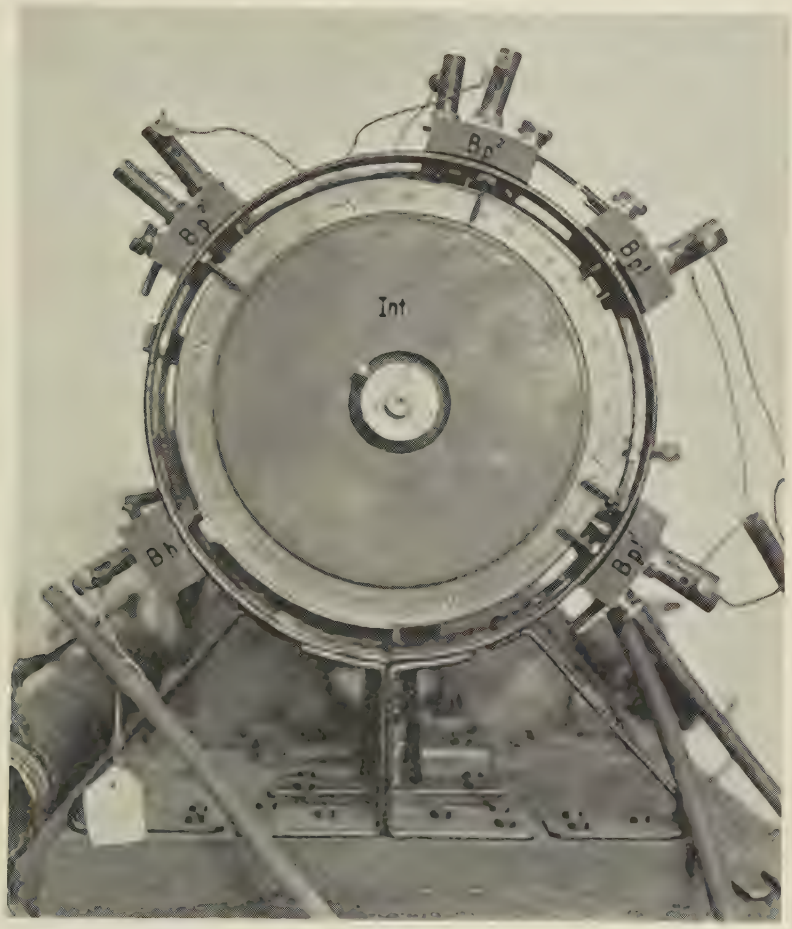

FIG. 3
End view of one disk of commutator.

creasing the speed of the interrupter. From the formula it is evident the time interval may be changed by decreasing or increasing the R.P.M. Several factors enter in, however, which place a limit upon the time-interval and still obtain reliable data. In the first place, as will be shown later, sufficient time must be allowed for the charge to reach a maximum during each charge interval. In the second place, the discharge potential at the instant the current is interrupted cannot be measured because the charging brushes

must have completely left the brass section of the interrupter before the potentiometer contact is made. This interval amounts to about 0.0001 second at 400 R.P.M. for the brushes used; and they are as thin (1 mm.) as other conditions will permit. In the third place, in order that the potentials shall be measured accurately to one millivolt the potentiometer circuit must be closed at least 0.0005 second. If, now, the electrode potential at the beginning of discharge is determined as soon as the apparatus will permit after the interruption of the current at the R.P.M. 400 and at a time interval just necessary for the potentiometer contact, the time during which the average potential is obtained is .0006 second. By assuming the average potential to be the actual potential at a time equal to half of the total interval, the shortest possible discharge interval at which potential can be measured is 0.0003 seconds after discharge has begun. These limitations are imposed by the very nature of equipment required in the commutator potentiometer method.

Among the advantages of the equipment used in this work not possessed by those previously used may be listed the following: (1) measurements may be made by both the direct and commutator methods at the same time; (2) both charging and discharging potentials may be measured at different and known intervals of charge and discharge without stopping the interrupter; (3) potentials can be determined as near the end of charge and beginning of discharge as the physical limitations inherent in the potentiometer commutator method will permit; (4) Anode, cathode and total potentials can be measured practically at the same time; (5) The I.R. drop between the electrodes may be measured directly; (6) Every individual potential throughout the charging circuit may be measured and their sum compared with the total potential delivered to the system; (7) Only one speed of the interrupter is required for a complete set of measurements.

Experimental

Hundreds of measurements were made with this outfit which were highly reproducible and satisfactory; but only a few typical sets are included in this report.

It was stated that the charge potential requires some time to reach a maximum value and that in a comparison of the direct and commutator methods care must be taken to see that sufficient time is allowed for the maximum to be reached. This is clearly evident from the curves of Fig. 4, where charge and discharge potentials are plotted against time from the beginning of the charge interval. Curves (a) and (a′) are the charge and discharge curves for a current density of 9 m.a., and (b) and (b′) for 90 m.a. For each set of curves the current density was held constant, also, the speed of rotation of the interrupter. Each point was determined by a separate set of brushes. Readings were taken in rapid succession and then repeated as a check. It was found advisable in all cases to pass a continuous direct current through the cell for at least half an hour before starting the interrupter. Measurements were not taken until the intermittent current had

been flowing about five minutes. These curves make clearly evident the following points. (1) It is possible, by means of the interrupter used, to obtain definite values for any part of either the charge or discharge interval and thus to plot a complete cycle. (2) The rate of charge and discharge at the various portions of the charge and discharge intervals depends upon the current density and is much greater at the start the higher the current density. (3) The time required to reach maximum charge is greater the lower the current density. (4) The only way to be certain the charge potential has reached its maximum value is to determine the charge curve.

The curves in Fig. 5 show the relation between current and cell potential as both change with time. The current increases much more rapidly than the potential and reaches a maximum after which it shows a slight but characteristic decrease as the potential increases.

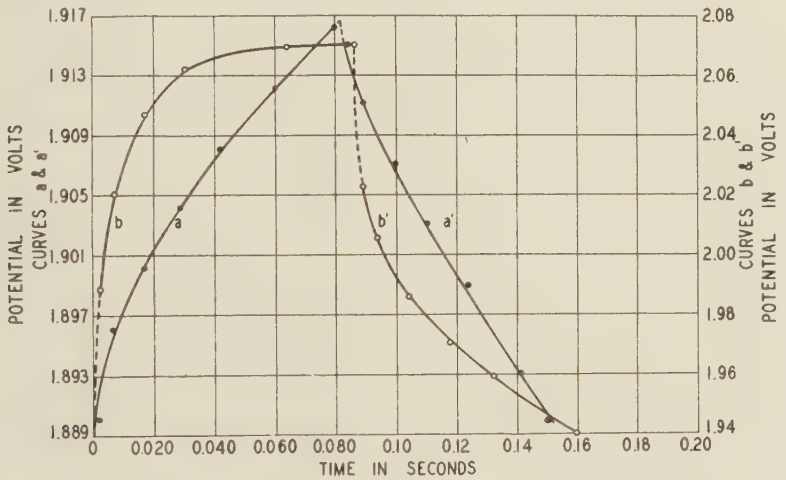

FIG. 4
Charge and discharge curves by commutator potentiometer method.

Attention was concentrated especially upon the portions of the curves at the end of charge and beginning of discharge as these are the parts which are of greatest interest and the portion which the redesigned commutator made it possible to study. The work reported earlier indicated that if measurements could be made close enough to the end of charge and the beginning of discharge the values would be found equal and thus proof furnished that there is no such thing as transfer or any other kind of surface resistance.

A typical set of data is given in Table II. The time in seconds recorded in column (1) corresponds to the interval after discharge has begun. Only one value for charge is recorded and that is for the time corresponding to 59° and is considered that at the end of charge since the charge had reached a maximum.

The average current density was determined by measuring the I.R. drop over a standard resistance during the total charge interval. Columns (3) and (7) contain the single electrode potentials at the end of charge minus the I.R.

drop through the connecting wires. The resistance of the electrode and connecting wire to the point where the potential was determined was in these experiments 0.24 ohms. The electrode potential values in columns (4) and (8), at zero time of discharge were obtained by extrapolation from the discharging curves. In each of the eight experiments, conditions were maintained constant except the current density which was made higher in each succeeding experiment. As the current density increases from 3.8 m.a. to 149 m.a.

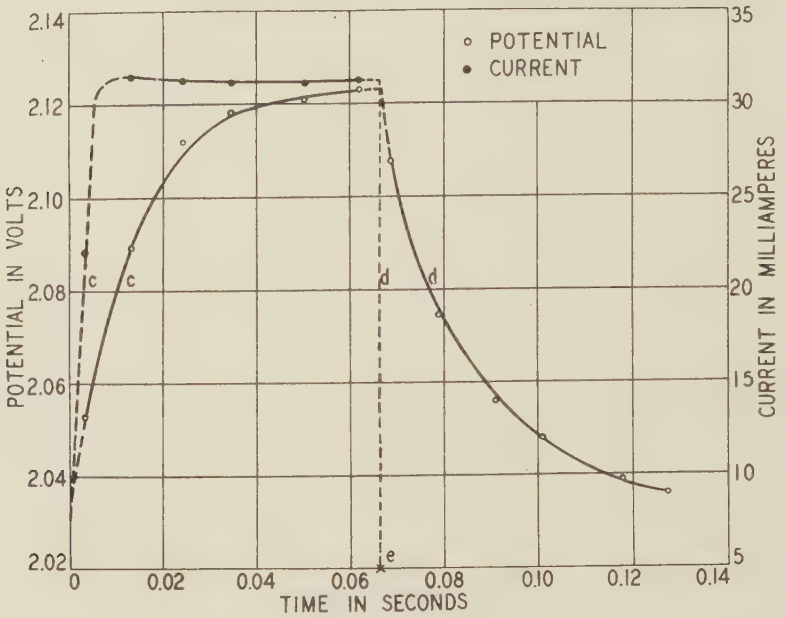

Fig. 5

Current and potential charge and discharge curves.

the polarisation of the cathode increases only 24 m.v. but the anode increases 282 m.v. The cathode drops two or three millivolts during the first few thousandths of a second then remains constant during the remainder of the discharge interval. The anode potential drops much more rapidly and continues to drop throughout the whole discharge interval. The anode potentials for some of the experiments are represented as curves in Fig. 6. The ends of the charge curves are represented as horizontal dotted lines since the potential had reached a constant maximum value. It should be noticed that the first point on the discharge curves was taken about 0.0008 sec. after the beginning of the discharge interval and the greatest extrapolation was only 9 m.v. The differences in potentials between the end of charge and zero time of discharge are given in columns (5) and (9). They amount to about 2 m.v. which is practically within the limits of experimental or extrapolation errors. This is the first time that anything like so close agreement has been found for such high current densities.

Table II

Relation between single electrode potentials on charge and on discharge at various current densities. Platinized electrodes. Time is in Sec. $\times 10^4$.

(1) Time $\times 10^4$	(2) $Pt.^+ - A.S.$ End of charge	(3) Pot. corr.	(4) $Pt^+ . - A.S.$ Discharge	(5) Pot. diff. m.v.	(6) $Pt.^- - C.S.$ End of charge	(7) Pot. corr.	(8) $Pt.^- - C.S.$ Discharge	(9) Pot. diff. m.v.
Experiment (1) Average C.D. = 0.0038								
0			1.040	−1			0.707	0
8			1.039				0.706	
40			1.038				0.705	
140			1.036				0.705	
460			1.032				0.705	
550			1.031				0.705	
590	1.039	1.039			0.707	0.707		
Experiment (2) Average C.D. = 0.0178								
0			1.165	0			0.722	−1
8			1.164				0.721	
40			1.162				0.719	
140			1.153				0.719	
460			1.138				0.719	
550			1.131				0.719	
590	1.167	1.165			0.723	0.721		
Experiment (3) Average C.D. = 0.0284								
0			1.210	−1			0.725	−2
8			1.209				0.724	
40			1.204				0.722	
140			1.193				0.722	
460			1.167				0.722	
550			1.161				0.722	
590	1.212	1.209			0.726	0.723		
Experiment (4) Average C.D. = 0.0436								
0			1.254	−1			0.728	−1
8			1.252				0.727	
40			1.246				0.725	
140			1.225				0.725	
460			1.197				0.725	
550			1.193				0.725	
590	1.259	1.253			0.723	0.727		

TABLE II (continued)

(1) Time × 10^4	(2) Pt.$^+$—A.S. End of charge	(3) Pot. corr.	(4) Pt.$^+$—A.S. Discharge	(5) Pot. diff. m.v.	(6) Pt.$^-$—C.S. End of charge	(7) Pot. corr.	(8) Pt.$^-$—C.S. Discharge	(9) Pot. diff. m.v.
Experiment (5) Average C.D. = 0.0722								
0			1.272	−2			0.729	−1
7			1.268				0.728	
33			1.256				0.726	
129			1.231				0.726	
423			1.200				0.726	
506			1.193				0.726	
543	1.278	1.270			0.736	0.728		
Experiment (6) Average C.D. = 0.0936								
0			1.290	−2			0.729	−2
8			1.286				0.728	
40			1.272				0.726	
140			1.249				0.726	
460			1.210				0.726	
550			1.204				0.726	
590	1.299	1.288			0.738	0.727		
Experiment (7) Average C.D. = 0.1228								
0			1.296	+2			0.730	0
7			1.290				0.729	
32			1.277				0.727	
122			1.250				0.727	
400			1.210				0.727	
479			1.201				0.727	
513	1.313	1.298			0.745	0.730		
Experiment (8) Average C.D. = 0.1490								
0			1.322	+2			0.731	+1
7			1.313				0.730	
33			1.293				0.729	
129			1.264				0.729	
423			1.220				0.729	
506			1.214				0.729	
543	1.342	1.324			0.750	0.732		

These data confirm the prediction made in an earlier paper that the potential at the beginning of charge and the end of discharge would be found equal if reliable measurements could be made. This means that transfer resistance or any other kind of resistance is not present at the surface of electrodes for the system just described.

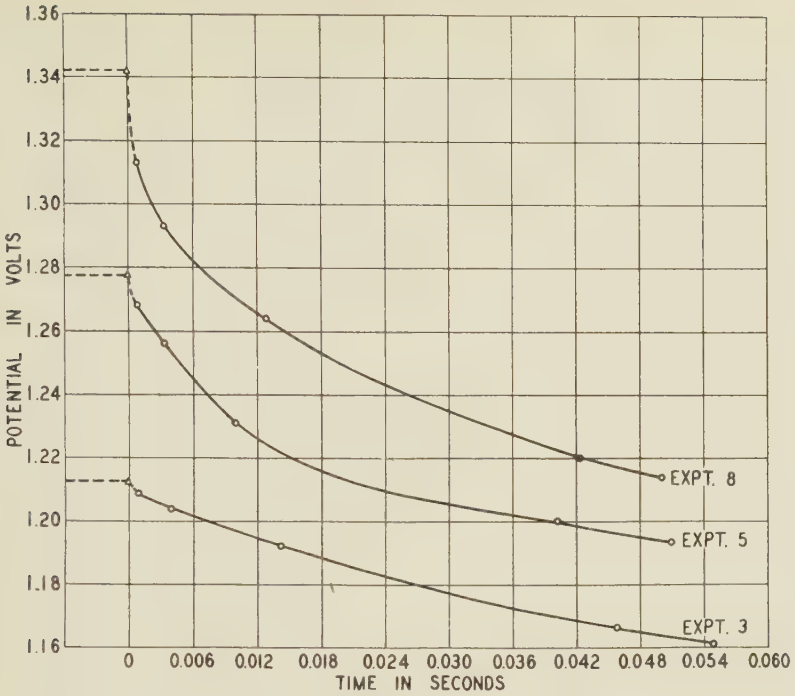

FIG. 6
Anode discharge curves for platinized electrodes.

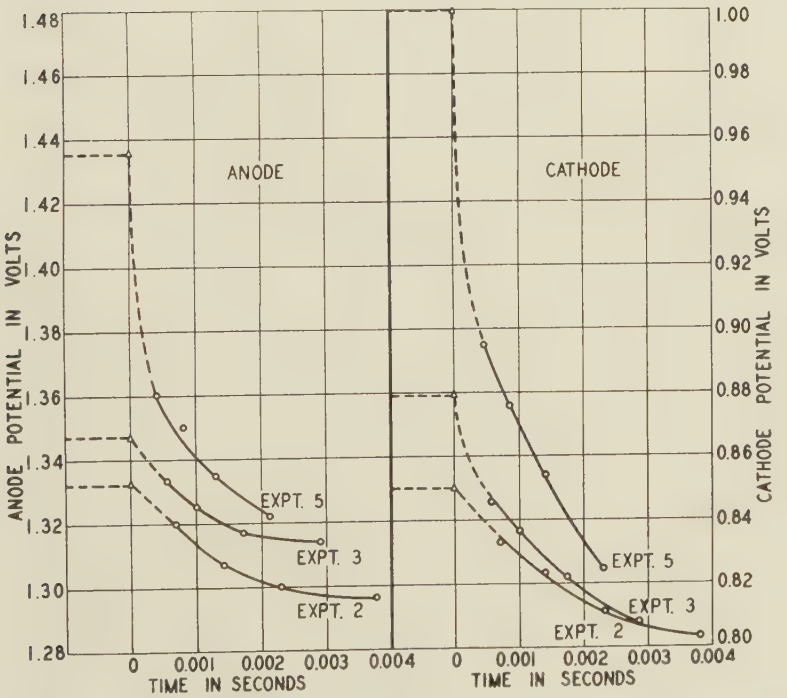

FIG. 7
Anode and cathode discharge curves for bright platinum electrodes.

TABLE III

Relation between single electrode potentials on charge and on discharge at various current densities. Smooth platinum electrode.

(1) Time $\times 10^{-4}$	(2) $Pt.^{+}-A.S.$ End of charge	(3) Pot. corr.	(4) $Pt.^{+}-A.S.$ Discharge	(5) Pot. diff. m.v.	(6) $Pt.^{-}-C.S.$ End of charge	(7) Pot. corr.	(8) $Pt.^{-}-C.S.$ Discharge	(9) Pot. diff. m.v.
Experiment (1) R.P.M. = 210, Average C.D. = 0.0001								
0			1.183	0			0.689	1
8			1.182				0.688	
15			1.181				0.688	
24			1.181				0.688	
40			1.181				0.687	
470	1.183	1.183			0.690	0.690		
Experiment (2) R.P.M. = 220, Average C.D. = 0.0016								
0			1.333	1			0.850?	0?
7			1.320				0.833	
14			1.307				0.824	
23			1.300				0.811	
38			1.296				0.803	
443	1.332	1.332			0.850	0.850		
Experiment (3) R.P.M. = 290, Average C.D. = 0.0026								
0			1.347?	0?			0.862?	17?
5.7			1.333				0.846	
10			1.325				0.837	
17			1.317				0.822	
29			1.314				0.807	
336	1.347	1.347			0.879	0.879		
Experiment (4) R.P.M. = 400, Average C.D. = 0.0360								
0			1.366?	20?			0.892?	24?
4			1.355				0.855	
8			1.344				0.833	
13			1.335				0.821	
21			1.325				0.811	
248	1.390	1.386			0.920	0.916		
Experiment (5) R.P.M. = 360, Average C.D. = 0.0500								
0			1.380?	49?			0.920?	74?
4.6			1.360				0.895	
8.3			1.350				0.876	
14			1.335				0.854	
23			1.322				0.825	
271	1.435	1.429			1.000	0.994		

Measurements were next carried out with smooth platinum electrodes. The data are recorded in Table III, and some are represented as curves in Fig. 7. A comparison of the data in Table III with those in Table II shows some pronounced differences. This is especially noticeable for the cathodes. While the platinized cathode increased in potential only 24 m.v. for a change in current density from 3.8 m.a. to 149 m.a., the smooth platinum changed about 200 m.v. for a current density change from 0.1 m.a. to only 50 m.a. The smooth platinum anode, on the other hand showed a considerably smaller change with current density than the platinized anode. The rate of decrease in potential on discharge was much greater for both anode and cathode with smooth than with platinized platinum, and here again the rate of decrease was much greater for the cathode than for the anode. At extremely low current densities smooth and platinized electrodes for both electrodes do not show these abnormal effects. It is clearly evident from the curves that, even though the first points on the discharge curves were obtained only about 0.0004 sec. after discharge started the potential had dropped probably 50 to 75 m.v. This is much too great a rate of change for safe extrapolation to zero time. This means that the commutator potentiometer method can not be relied upon to give satisfactory results for smooth platinum electrodes.

Summary

1. A commutator was used which enabled potentials to be measured within 0.0005 sec. from end of charge or beginning of discharge.

2. The system permitted the measurement of every potential drop in the complete circuit, and their sum could be compared with the source potential.

3. Measurements were made for anode, cathode and total potentials at several points on the charge and discharge intervals, practically simultaneously, without stopping the interrupter, so that curves could be plotted for complete cycles.

4. It was proven that for platinized electrodes in two-normal sulfuric acid there is no surface resistance of any kind for current densities between 3.8 and 150 m.a.

5. With smooth platinum electrodes the decrease in discharge potential is so rapid that satisfactory results can not be obtained with the interrupter potentiometer system.